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Instrumentation for High-Density Patterning of Upconversion Nanoparticles and Peptide-based Nanobioassemblies

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14. ABSTRACT
With the TERA-Fab E series, we aim at exploring a high-density large-area patterning of photoactive nanocrystals and peptide-based nanomaterial which could play a crucial role in the development of novel hybrid materials and components. Graduate students and post-doctoral researchers are actively involved in all of these research programs; access to the proposed state-of-the-art instrument will enhance their educational experience in photonics and materials science, areas of key AFOSR interest. The instrument greatly expands our current abilities. Furthermore, it will allow for the training of students in advanced micro- and nano-patterning techniques. Such training will educate these future scientists and engineers in disciplines important to the DoD mission; such skills could be readily translatable to research geared toward combinatorial biological and materials science experiments, integrated nanoelectronics and photonics, and high sensitivity chemical and biological detection tools.
A.1. Instrument installation at ILPB in University at Buffalo
The TERA-Fab E series was installed at April 26, 2018, at ILPB (See figure 1a), and two graduate students and three research faculties were trained for the first use of the instrument in Beam-Pen Lithography (BPL) mode. The BPL combines the advantages of Polymer-Pen Lithography (PPL) and near-field scanning optical microscopy (NSOM). A typical BPL array is fabricated by coating a traditional PPL array with an opaque metal (i.e., gold) and then opening apertures at the tips of the coated pens. This allows for the generation of arbitrary patterns with features smaller than the wavelength of incident light. Individual pens can be addressed by using a digital micromirror device (DMD). By using the DMD, much like PPL, this technique is scalable with as many as hundreds of thousands of tips being individually addressed at once.

15. SUBJECT TERMS
TERAFab E-series dual Polymer Pen Lithography, Beam Pen Lithography, nanobiocombinatorics, core-shell nanoparticles

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peptide-based nanomaterial which could play a crucial role in the development of novel hybrid materials and components.

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proposed state-of-the-art instrument will enhance their educational experience in photonics and materials science, areas of

key AFOSR interest. The instrument greatly expands our current abilities. Furthermore, it will allow for the training of students

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fabricated by coating a traditional PPL array with an opaque metal (i.e., gold) and then opening apertures at the tips of the

coated pens. This allows for the generation of arbitrary patterns with features smaller than the wavelength of incident light.

Individual pens can be addressed by using a digital micromirror device (DMD). By using the DMD, much like PPL, this

technique is scalable with as many as hundreds of thousands of tips being individually addressed at once.

A.2. Patterning of perovskite quantum dots on FTO glass

To demonstrate the patterning capability of the TERA-Fab E series, a pattern of perovskite quantum dots was fabricated on a

conductive fluorine-doped tin oxide (FTO) glass in the BPL mode. The perovskite quantum dots (QDs), cesium lead bromide

(CsPbBr3), were prepared by colloidal hot casting procedure which is adding Cs-oleate into PbBr2 solution containing oleic

acid, oleylamine, and octadecene at high temperature. We obtained brightly green emissive CsPbBr3 QDs and mixed them

with a solution of negative photoresist to prepare a precursor for photo patterning. The precursor was coated on a FTO glass

by spinning, and then we patterned a logo of the University at Buffalo (UB) with 410 nm light by the beam-pen-lithography

method. After the removal of the unpatterned part by solvent washing, we imaged the film on FTO with SEM and confirmed a

clear pattern of UB logo (See figure 1b). Then we imaged fluorescence from the pattern and analyzed the emission spectra in

a broad visible region near 530 nm from the fluorescent pattern and dark background, respectively (See Figure 1c). The

strong 530 nm emission spectrum on the pattern was well accorded with the original emission spectrum from the QDs. As a

result, we demonstrated the potential of the TERA-Fab E series for patterning perovskite quantum dots without any

unexpected change in the intrinsic optical properties. Also, with this demonstration, our researchers and students were getting

trained more for further patterning studies.

A.3. Future work: Nano-pattering of peptide-based nanobioassemblies

For further study, as we proposed, we will pattern peptide-based nanobioassemblies which are hybridized by selective peptide-nanoparticle interactions. For this, a monolayer of cis-azobenzene molecules will be prepared, and a selective photopatterning

will be conducted to produce an arbitrary arrangement of trans-azobenzenes, which have a superior association

constant (roughly 2500 M-1) with cyclodextrin (CD) compared with cis-azobenzene (non-quantifiable). This will allow us to

deposit NPs and their assemblies at specific positions by host-guest chemistry (See Figure 2), providing a patterned

foundation layer for growth of 3D assemblies. This large-area directed assembly of a surface pattern complements the selfassembly

approach achievable via host-guest chemistry of peptide-capped NPs described above. With the 3D pattern of

peptide-based nanobioassemblies which will be obtained by photopatterning with TERA-Fab E series, we will explore their

plasmonic, optoelectronic, and nonlinear optical properties at a various combination of nanopatterns and nanomaterials.